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An Investigation of the Degradation of Ceramic Coatings on Metals using a Microwave Technique

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1. INTRODUCTION

Metal components for use in high temperature oxidising or corrosive environments often require protection. Many of the coatings used are complex but the two basic types are as shown in figure 1. In type A, source material is diffused into the surface of the component. When heated in air some of the source material oxidises to form a thin protective ceramic layer. The coating continues to be protective as long as there is an adequate supply of source material to provide new ceramic to replace any lost from the surface. Any non-destructive testing system for such a coating must give information on the amount of source material in reserve. In system B (figure 1) the relatively thick ceramic coating is applied as a slurry or is sprayed on by flame or plasma arc. The ceramic gives erosion corrosion and thermal protection. Owing to the porosity of the ceramic oxidation/corrosion of the protected metal will eventually take place. This attack is the preliminary stage to separation of the ceramic from the metal and also to failure of the metal component. Non-destructive testing must give information on the interfacial region between ceramic and metal.

The following systems are of current interest and have been investigated in simplified forms:

(a) aluminised Nimonic - prevention of sulphur corrosion in Nimonic gas turbine blades

(b) disilicide coated Niobium - possible development of satisfactory protective coatings for refractory metals

(c) ceramic coated mild steel - heat shields and rocket nozzles.

2. BASIC MEASUREMENT TECHNIQUE

The 'Q' factor of a resonant microwave cavity is determined by the energy lost from the cavity. The principal losses are energy radiated from the cavity through coupling holes, and the energy dissipated in the walls of the cavity. This latter loss is due to the finite conductivity of the material of the walls. Electric currents flow in the walls of the cavity but only penetrate a short distance below the surface. The depth of penetration decreases with increasing microwave frequency

and decreasing resistivity of the material.

The ceramic (figure 1) in both types of coating is an insulator and therefore transparent to microwave radiation. If a sample of coated material is made one wall of a microwave cavity (figure 2), the effective wall is the outer layer of the metal, which for a type A coating is the region rich in source material and for type B is the interfacial region. Measurement of cavity 'Q' should yield information on the electrical resistivity of the important region in the coatings.

3. MICROWAVE APPARATUS

The electrical resistivity of metals at room temperature is commonly between 1μΩcm and 20μΩcm; alloys and intermetallic compounds have resistivities up to 1000μΩcm and semiconducting oxides up to 1Ωcm. Samples of coated metals are most easily prepared as flat plates. Although many possible measuring techniques are available that of Seaman (1943) and Bussey(1960) is most readily applicable to the above conditions.

A microwave cavity resonant in the H_{011} circular mode was chosen as this mode does not require electrical contact between the end plate, and the cylindrical walls of the cavity. A working frequency of 25Gc/s resulted in a reasonably sized cavity. The effect of the degenerate E_{111} mode was minimised by:

(a) arranging the input and output guides to be at 90° to each other

(b) leaving 0.010" clearance between the tuning plunger and its tube and providing absorbing material round the shaft of the plunger.

It was possible to tilt a specimen so as to give up to 0.003" clearance at one side of the cavity without appreciable change in 'Q'.

The klystron (figure 3) was frequency locked to a standard reference cavity using a Pound (1947) stabiliser and the resonance curve of the measuring cavity displayed by tuning the measuring cavity. This method was preferred to tuning the klystron as it did not require a broad band detecting system. The 'Q' of the

measuring cavity was about 5000 with an annealed copper sample and fell to about 50 with a 1Ωcm semiconductor.

The apparatus was calibrated against materials of known resistivity. The power transmitted by the cavity depends on its 'Q'. Samples were placed on the measuring cavity, the cavity tuned to give maximum power transmitted and the standard attenuator adjusted to give a standard reading on the meter MI. (See also section 5).

4. APPARATUS SENSITIVITY

For a medium whose resistivity is ρ, magnetic permeability μ, and dielectric constant ε, Maxwell's equations become

$$\nabla \times E = -\mu\mu_o \frac{\delta H}{\delta t} \qquad \nabla \times H = \varepsilon\varepsilon_o \frac{\delta E}{\delta t} + \frac{E}{\rho}$$

$$\varepsilon_o \nabla . \varepsilon E = 0 \qquad \mu_o \nabla . \mu H = 0$$

where ρ, μ and ε can be functions of x, y and z. In the very limited case of a plan polarised wave incident normally on an infinite plane conductor of larger thickness and with homogeneous isotropic properties the solution of the equations is simple (see any standard text) and yields the results:

(a) the transmitted wave is rapidly attenuated, falling to 1/e of its initial value in the skin depth δ_o where

$$\delta_o = (\pi \mu_o f . \frac{\mu}{\rho})^{-\frac{1}{2}} \qquad (1)$$

(b) the conductor has an intrinsic impedance Z where

$$Z = (1 + j)\sqrt{2\pi f \mu_o \mu \rho} \qquad (2)$$

(c) the apparent wavelength in the conductor λ' is

$$\lambda' = 2\pi\delta_o \qquad (3)$$

The 'Q' of any resonant system is made up of several components such that

$$\frac{1}{Q_L} = \frac{1}{Q_1} + \frac{1}{Q_2} + \frac{1}{Q_3} + \ldots\ldots \qquad (4)$$

where Q_L is the observed Q of the resonator

Q_1, Q_2 etc. are the contributions due to the various forms of energy loss from the resonator.

The contribution Q_1 due to energy loss in the walls of a microwave resonator is

$$\frac{1}{Q_1} = \text{Real part} \sum_{i=1}^{n} \left(\frac{Z_i}{\pi f \mu_o}\right) \frac{S_i'}{2V'} \qquad (5)$$

(Bethe 1943). Where the cavity is made from n components each with intrinsic impedance Z_i

$$S_i' = \int_{S_i} |H_1|^2 dS \qquad V' = \int_V |H_1|^2 \, dV$$

If one part of the cavity wall is replaced by another with slightly different resistivity

$$\frac{\partial}{\partial \rho}\left(\frac{1}{Q_1}\right) = \frac{1}{\pi f \mu_o} \cdot \frac{\partial}{\partial \rho}(Z_i) \cdot \frac{S_i'}{2V'}$$

Hence from equations (2) and (6)

$$\frac{\partial}{\partial \rho}\left(\frac{1}{Q_1}\right) = \sqrt{\frac{\mu}{2\pi f \mu_o \rho}} \cdot \frac{S_i'}{2V'} \qquad (6)$$

and the change $\delta\rho$ which corresponds to a change of δQ in Q_L is given by

$$\delta\rho = -\frac{1}{Q_L} \cdot \frac{2V'}{S_i'} \sqrt{\frac{2\pi f \mu_o \rho}{\mu}} \cdot \frac{\partial Q_L}{Q_L}$$

From an H_{011} made cavity where S_i' refers to the end plates

$$\frac{2V'}{S_i'} = \frac{4L}{\lambda_o}$$

where L = length of cavity

λ_o = free space wavelength of radiation where frequency is the resonant frequency of the cavity.

Therefore

$$\delta\rho = -\frac{1}{Q_L} \cdot \frac{4L^3}{\lambda_o^2}\sqrt{\frac{2\pi f \mu_o \rho}{\mu}} \quad \frac{\delta Q_L}{Q_L} \qquad (8)$$

For maximum sensitivity L must be as small as possible subject to maintaining a large value of Q_L.

The cavity used in the measurements had an internal diameter of $\frac{7}{8}$ inches and length $\frac{5}{16}$ inches. Q_L when the sample was a copper plate ($\rho = 1.9 \times 10^{-6}\Omega$cm) was approximately 5000 and could be measured to 1%. From equation (8) $\delta\rho = 0.16 \times 10^{-6}\Omega$cm, i.e. ρ can be measured to 8%.

As the resistivity of the specimen increased it became the dominant source of loss in the cavity and $Q_L = Q_1$.

Substituting from equations (2) and (5) into equation (8) gives

$$\delta\rho = 2\rho \frac{\delta Q}{Q}$$

As the 'Q' could still be measured to 1%, ρ could be measured to 2%. For most of the samples investigated the resistivity was much larger than that of copper hence most resistivities could be determined to 2%.

These calculations assume that the specimen can be replaced accurately enough on the microwave cavity for there to be no significant changes in 'Q' due to change in specimen location. Twelve pieces of brass plate were cut from the same sheet and surface ground. The resistivity of each sample was measured several times on the microwave apparatus using various orientations of the grinding marks to the input and output waveguides. The maximum deviation of resistivity from mean value was 30% and the standard deviation was 10%. There was no systematic error. As most of the coated specimens had neither the flatness nor the quality of surface finish of the brass it would appear that in general resistivity was determined to not better than 15%.

5. APPARATUS CALIBRATION

The equivalent circuit of the microwave transmission circuit used in the apparatus is shown in figure 4(a). This circuit transforms into the single loop equivalent circuit (figure 4(b)) where the power Po coupled into the detector is -

$$Po = \frac{n_1^2 n_2^2 RoE^2}{(n_1^2 Ro + n_2^2 Ro + R)^2} \cdot \frac{n_1^2 n_2^2 Ro Q_L^2 E^2}{\omega^2 L^2} \qquad (10)$$

where $Q_L = \frac{\omega L}{n_1^2 Ro + n_2^2 Ro + R}$ = 'Q' of cavity.

If the microwave apparatus is operated so as to maintain the output power constant by varying the voltage E at the generator, from (10)

$$\frac{1}{Q_L} \propto E \qquad (11)$$

Substituting from equations (3), (4)and (6) leads to a result of the form

$$\sqrt{\rho} = AE + B \qquad (12)$$

where ρ = resistivity of the specimen A and B are constants.

In the practical circuit (figure 3) the generator voltage was controlled by the standard attenuator.

Figure 5 shows a typical calibration curve for the apparatus where metals and alloys of known low frequency resistivity have been used as standard samples. A sample with a resistivity of 1Ωcm was also available. When the results of figure 5 were extrapolated to 1Ωcm the measured and extrapolated values differed by only 15% which was very satisfactory agreement over 6 orders of magnitude of resistivity.

6. DEGRADATION OF DISILICIDE COATED NIOBIUM

6.1 Material and test procedure

Twelve samples of commercially pure niobium $1\frac{1}{4}$ x $1\frac{1}{2}$ x .030 were coated at 1050°C in a fluidised bed of silicon powder by N.G.T.E. Pyestock, England. The resulting disilicide coating was from 52μm to 59μm thick pale grey in colour with a uniform fine matt surface texture except for a small number of blotches or splashes. The coating was appreciably thicker beneath the splashes.

The resistivity of the disilicide coating on the samples when received varied from 100μΩcm to 190μΩcm with a mean value of 136μΩcm. The low frequency resistivity of $NbSi_2$ is 50.4μΩcm (Samsonov 1966). A slightly cracked disc of $NbSi_2$ when measured on the microwave apparatus showed a resistivity of 74μΩcm. The large value of resistivity observed in the coatings could be due to variations in composition and/or cracks in the coating.

The samples were tested by heating in a tube furnace through which passed a slow moving current of air. The temperature in the furnace was measured with a thermocouple placed close to the sample. The samples were removed from the furnace and cooled to room temperature at intervals for measurement.

6.2 Results

Neglecting samples that failed prematurely as a result of local defects in the coating, the results for 1250°C are shown if figure 6. The resistivity results showed two distinct regions; (a) where the resistivity remained substantially constant during the first few hours (b) where a rapid rise occurred, culminating in failure. These two regions were associated with two different stages in the degradation of the coating. When first heated to a high temperature a dark grey, glassy coating formed on top of the disilicide layers. This glassy layer was well defined at temperatures in excess of 1400°C but not so obvious on samples exposed to lower temperatures. This outer layer was crazed with individual blocks (about 0.5 mm. across) separated by hairline cracks. On further exposure to high temperature attack began at the base of these hairline cracks. The disilicide at the base of the crack in the silica was converted to a yellow powder. At this intermediate state the surface appeared as a mozaic of grey blocks separated by cracks filled with yellow powder. Attack did not proceed vertically into the disilicide layer but rather horizontally at the interface of glassy layer and disilicide.

Eventually a complete yellow layer formed between glass and disilicide and as the yellow material had little mechanical strength, the glassy layer then flaked off. This change in the outer surface from glass to yellow powder coincided with the change from region (a) to region (b) in the resistivity results. From this point onwards the disilicide layer was apparently consumed to form more of the yellow material and this growth was associated with the rapid rise in resistivity. Eventually the disilicide layer was completely consumed and the specimens failed completely.

Some of the yellow powder from a sample which had been on test for 34 hours at 1250°C was subject to X-ray diffraction analysis. The principal constituents were found to be α-Nb_2O_5, Nb_2O_5 and NbO_2 with traces of $NbSi_2$. (Table 1).

The processes taking place in specimens held at 1000°C were identical with those in the 1250°C specimens except that the time scale was much longer (figure 7). Because of the very long exposure period, failure due to small defects in the coating was more common than in the 1250°C specimens. All the specimens tested failed from the consequences of pinhole defects before the resistivity had reached the very high values recorded on the 1250°C samples.

Similar results were obtained with specimens held at 1450°C but the composition of the yellow layer may have been slightly different as the yellow material was much less adherent and flaked off more readily as the specimens were cooled. The loss took place regardless of rate of cooling. As the steep rise in the observed resistivity was undoubtedly due to the increasing thickness of the yellow layer not to changes in the bulk resistivity, observed values were lower when material was lost. Because of this loss the transition from (a) region to (b) region in the resistivity curves was not observed until some time after the yellow layer had started to form at 1450°C and recorded rise is smaller than if there had been no loss. The complete yellow layer first formed after about 4 hour exposure, not 7 hours as indicated by the graph (figure 8).

6.3 Mode of failure of specimens

Failure as a result of local defects has been considered in detail by Perkins (1965) and by Restall (1967). The present resistivity measurements are not suitable for studying this type of failure.

When a specimen was first heated in air a protective layer of silica formed on the outside while the outer layers of disilicide were degraded to a lower silicide. If the temperature had been high enough and/or the heating period long enough, diffusion within the disilicide layer would have substantially restored the silicon concentration in the outer layers. In the present experiments it appears that the diffusion rate was too small so that when the specimen was cooled the inevitable cracks in the silicon exposed the lower silicides to attack (figure 9). These lower silicides do not form a protective silica layer. On further heating, attack proceeded transversely below the silica layer which eventually flaked off leaving an outer surface composed of niobium oxides. As this layer of oxide thickened very rapidly apparently at the expense of the disilicide, it appears that diffusion of niobium from below was not important. Evidently it was impossible for a new protective silica layer to form below the niobium oxides. Electron probe microanalysis showed a high silicon concentration in the niobium oxide layer which confirmed that growth was largely at the expense of the disilicide.

7. OXIDATION OF MILD STEEL AND PROTECTED MILD STEEL

7.1 Effective resistivity

The microwave apparatus compared the intrinsic impedance of surfaces. If a material resistivity ρ_1 permeability μ_1 gave a reading R_1 on the apparatus and a second material ρ_2, μ_2 gave reading R_2^1 then

$$\sqrt{\frac{\mu_1 \rho_1}{\mu_2 \rho_2}} = \frac{R_1}{R_2}$$

The materials so far considered and also those used for calibration had $\mu = 1$ and hence the apparatus compared their resistivities. Mild steel and its oxides are generally ferromagnetic, $\mu > 1$. When the readings from mild steel samples were compared with those from calibration materials an effective resistivity ρ^1 was obtained.

$$\rho^1 = \mu\rho$$

7.2 Unprotected mild steel

Measurements were made on unprotected mild steel in order to obtain values of the effective resistivity of mild steel and its oxides. Samples of mild steel were surface ground and then heated in a tube furnace in a slowly moving current of air. In some tests the samples were removed at regular intervals, cooled to room temperature and then replaced in the furnace. The effective resistivity was found to depend on the furnace temperature, total time in the furnace and the number of heating cycles in this total time. Figure 10 shows typical results for such a sample. During the earlier cycles gross spallation took place and this may well have been the cause of the peak in the curve. The effective resistivity of a thin conducting film raised some distance from the end plate of the microwave cavity is very high. After further cycles the oxide became more closely bonded and the effective resistivity fell.

If the samples were heated continuously at a steady temperature with no recycling, the effective resistivity was much lower and more reproducible. Table 2 gives the steady state effective resistivities after sufficiently long heating periods. From the known oxidation behaviour of mild steel, the resistivity of oxides formed below 570°C can be expected to be very different from that of oxides formed at higher temperatures.

7.3 Mild steel protected solely by ceramic

Some samples of mild steel were given aluminium phosphate bonded coatings of types IC123 and IC109F (N.A.S.A. Technical Note D 106). Further samples were grit blasted with 40 mesh grit and then flame sprayed with up to 0.010" of alumina (Rokide A). All samples were heated using a propane/air torch with sufficient excess air to give a strongly oxidising flame. The flame was incident normally on the ceramic and the temperature of the rear face of the mild steel was monitored with a thermocouple welded to the steel. Samples were heated to various temperatures from 500°C to 1000°C. The mild steel was 0.25 thick. On some samples the ceramic coating separated from the mild steel as a result of thermal shock on others by the formation of a thin oxide layer between the mild steel and the ceramic. This oxide appeared to remain bonded to the ceramic but not to the mild steel. No significant change in microwave resistivity was observed before the separation of the coating.

7.4 Mild steel protected by metal plus ceramic

The protective coating recommended by Metallization Ltd., Dudley, England, consisted of 0.001" to 0.002" of Nichrome flame sprayed on to the grit blasted mild steel, followed by up to 0.040" of Rokide A. Such coatings were tested as described in section 7.3. Again no changes in microwave properties were detected but the results were not conclusive. Failure was the result of oxidation of the unprotected mild steel at the back and edges of the samples, not failure of the coating. This coating system might repay further investigation using fully protected samples.

8. DEGRADATION OF ALUMINISED NIMONIC 105

8.1 Materials

The material used in all the tests was EPK26, the sheet version of Nimonic 105. Samples 1½" x 2" were cut from .070" sheet and heat treated for 30 minutes at 1100°C followed by 4 hours at 850°C, both in air. Some of the samples were pack aluminised by Rolls Royce Derby, in accordance with British Patent No. 16676/65; others were aluminised by Bristol Siddeley Engines Ltd., Bristol. Some of these latter samples had been given a post aluminising heat treatment of 1 hr at 1100°C in argon followed by 4 hrs at 850°C in air.

8.2 Resistivity and appearance of samples after aluminising

The samples from Rolls Royce had been polished. They were silvery in appearance except for darker grey areas on some of the faces. All the samples had one face with an appreciably higher resistivity than the other. The mean resitivity of the low resistivity faces was 110μΩcm with a standard deviation of 21μΩcm. The high resistivity faces had a mean value of 152μΩcm, standard deviation 2μΩcm. No information was available on how the specimens had been mounted for pack aluminising but it would appear that one face received greater exposure than the other on all specimens. Further measurements of resistivity were made using a conventional eddy current technique operating at 27 mc/s. These measurements gave a mean resistivity of 114μΩcm, standard deviation 4μΩcm, and no significant difference between faces. The differences between faces must have been confined to the outermost regions.

Twelve samples coated by Bristol Siddeley had only been aluminised. These samples varied from white to dark grey in colour. Most samples showed the same resistivity on both faces but there was a wide variation in resitivity from sample to sample; the whiter the sample, the lower resistivity. Resistivity values ranged from a minimum of 54μΩcm to maximum of 217μΩcm with a mean value of 107μΩcm. A further twelve samples had received the post aluminising heat treatment. Again there was a wide variation from sample to sample but little difference between the faces of each sample. The minimum resistivity was 130μΩcm, and maximum was 428μΩcm with a mean value of 208μΩcm. It was claimed by Bristol Siddeley that the post aluminising heat treatment gave a reduction in hardness and a readjustment of the phases present. The effect on the resistivity was apparently to cause an increase and to widen the variation from sample to sample. According to Llewellyn (1967) the principal constituent of the heat treated coatings should be aluminium rich NiAl. Yamaguchi et al (1968) have measured the electrical resistivity of such alloys and found a marked variation of resistivity with composition but their resistivity values (in the range 10μΩcm to 40μΩcm) are much lower than those found in the coatings.

8.3 Degradation of Rolls Royce aluminised samples at 1200°C and 1000°C

The samples were heated in long tube furnaces through which passed slow currents of air. Except for the first few hours when more frequent observations were made, the samples were withdrawn from the furnaces once every hour for a period of 10 minutes and allowed to cool in air. At intervals the samples were completely removed from the furnace environment, cooled to room temperature and measured on the microwave apparatus.

Figure 11 shows the changes in the resistivity of the 1200°C sample that took place in the first few hours. Before heating one face of the sample was silvery while the other had a grey region covering about half the area. When heated the silver face became covered with a rough granular layer of white alumina. From the work of Llewellyn (1967) and Goward (1967) one would expect a change from aluminium rich NiAl to nickel rich NiAl in the coating. According to the results of Yamaguchi (1968) this change in composition should be associated with a fall and then a rise in the electrical resistivity. In form, the resistivity results on the silver face agree with these predictions. The face with the grey area showed no such changes in resistivity. The alumina which formed over the grey area had a green tinge.

After the first few hours both faces of the 1200°C specimen had approximately the same resistivity until at 300 hours exposure the resitivity of the grey face began to vary markedly from place to place. The maximum variation recorded was 580 cm in the coloured area and 184 cm just outside it after the specimen had been on test for 2100 hours. Not only were there these wide variations from place to place but also with time, so that results on the initially grey face have proved worthless. A further feature of this face was the appearance of bright blue craters within the coloured area after 470 hours exposure. These craters increased in number and to a lesser extent in size during the test.

The initially silver face behaved more simply (Figure 12), without the large variations in resistivity over short periods or from place to place. According to metallographic evidence (Llewellyn 1967, Goward 1967) one would expect the replacement of the NiAl in the coating by Ni_3Al. There is a minimum in the resistivity versus composition curve at Ni_3Al (Starke 1965). It is not therefore surprising that the resistivity versus time graph (figure 12) first levels off and then begins to fall. Unfortunately a fault in the temperature control mechanism of the furnace caused the loss of the sample after 2100 hours.

The long term changes in the sample held at 1000°C (figure 13) were similar to those in the sample at 1250°C except for a slightly longer time scale. This sample also had a grey area on one face but it did not show the wildly erratic beheaviour of the 1250°C sample. Some blue craters developed in the grey area but not to the extent seen at 1250°C. After 2000 hours exposure the resistivity was found to vary considerably from place to place on the specimen and shortly afterwards pinholes developed in the coating. These pinholes grew in size and gradually the specimen became so damaged that further measurements were impossible. Because of the large size of the measuring cavity in comparison with the sample and the defects that developed, no really meaningful topographical survey of resistivity was possible but it appeared that regions which failed rose to a very high resistivty, 3600μΩcm was once recorded, and then fell to a very low value, possibly below 100μΩcm.

8.4 Degradation of samples at 1300°C

From the work of Goward (1967) it appeared that the changes in aluminised Nimonic should be similar at 1300°C to those at lower temperatures but should take place in a shorter time. Figure 14 shows typical results for a sample held at 1300°C and in form they are similar to those for lower temperatures (figures 12 and13). As at lower temperatures, some faces of samples showed

large variations in resistivity from place to place and failure wasuusually associated with a peak in the resistivity versus time curve. The coating on the Rolls Royce samples tended to melt and flow leaving a surface covered with fine ripples which made measurements difficult. Annealing for periods of up to 48 hours at 1200°C partly overcame this problem. The Bristol Siddeley samples did not appear to suffer from surface melting, which suggested that either the aluminium concentration was slightly different in the two coatings or that one of them had additives.

8.5 Discussion and Conclusions

No account has been taken of magnetic properties in the measurements on Nimonic 105. Certain alloys of nickel, aluminium, chromium and cobalt are ferromagnetic and consequently the resistivity values are more likely to be "effective resistivity" as defined in section 7.1. This may account for the large difference between the microwave resistivity of nickel-aluminium coatings and the reported d.c. resistivity of nickel-aluminium alloys.

It appears that before the coating fails there is a very large rise in resistivity followed by an equally large fall but these changes may only affect a small region of the sample. As with all coatings failure is a local effect rather than a general one. Measurements using a small sized probe would apparently detect regions of possible failure but whether measurements of the average resistivity over large areas would yield useful information is less clear.

9. GENERAL CONCLUSIONS

The technique described in this report is basically an eddy current testing technique and consequently suffers from the defects of all such techniques. The readings on the instrument are not a direct measure of any single effect within the test sample but require interpretation on the basis of experimental correlation between likely changes in the material and corresponding instrument readings. The difference between the microwave apparatus the more conventional eddy current devices is the very small depth of penetration in the microwave case which results in the instrument giving information about surfaces rather than bulk material.

In certain cases a clear correlation has been found between instrument readings and changes in the surface layers of coated materials. In aluminised Nimonic alloys the apparatus appears to give some advance warning of failure but a great deal more work is required to confirm theresults. The technique should be suitable for thestudy of other surface defects and may be a means of locating local residual stress, strain or damage which, in cyclically loaded components, could lead to fatigue failure.

TABLE 1 Analysis of Oxidation Products on Niobium Samples

(a) Observed diffraction pattern

Line No.	'd'	designation	
1	5.14	α-Nb_2O_5	
2	4.08	Nb_2O_5	
33	3.74	α-Nb_2O_5	
4	3.60	Nb_2O_5	αNb_2O_5
5	3.48	α-Nb_2O_5	NbO_2
			$NbSi_2$
6	3.34	Nb_2O_5	
7	2.82	Nb_2O_5	
8	2.69	Nb_2O_5	αNb_2O_5
9	2.54	NbO_2	
10	2.30	Nb_2O_5	
11	2.25	$NbSi_2$	
12	2.05	Nb_2O_5	
13	1.93	$NbSi_2$	
14	1.91	NbO_2	
15	1.81	Nb_2O_5	
16	1.78	NbO_2	
17	1.76	Nb_2O_5	NbO_2
18	1.58	Nb_2O_5	
19	1.40	Nb_2O_5	
20	1.36	$NbSi_2$	
21	1.30	Nb_2O_5	
22	1.28	$NbSi_2$	

TABLE 1

(b) Standard Patterns (Strong lines only)

NbO_2				αNb_2O_5		Nb_2O_5				$NbSi_2$	
d	I	d	I	d	I	d	I	d	I	d	I
5.63	20	1.975	20	5.13	20	3.77	15	2.10	75	3.52	72
4.29	20	1.932	20	4.63	20	3.71	55	2.05	55	2.587	32
3.63	30	1.897	20	3.75	70	3.63	80	1.98	100	2.255	100
3.42	100	1.862	20	3.74	50	3.56	15	1.84	40	2.199	35
3.21	30	1.829	20	3.65	100	3.49	75	1.76	40	2.079	21
2.91	30	1.766	30	3.49	50	3.36	55	1.700	75	1.941	64
2.54	80	1.754	80	2.78	20	2.82	15	1.695	75	1.358	22
2.49	30	1.712	50	2.71	20	2.77	15	1.598	55	1.355	25
2.42	50					2.70	15	1.59	50	1.277	13
2.34	20					2.55	15	1.567	50		
2.25	30					2.34	20	1.398	85		
2.166	20					2.32	20	1.190	65		
						2.28	75				

TABLE 2

Furnace Temperature °C	200	550	700	1000	1250
Effective Resistivity Ωcm	0.004	0.0019	0.0080	0.0064	0.0064

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Figure 1 Basic types of protective coating.

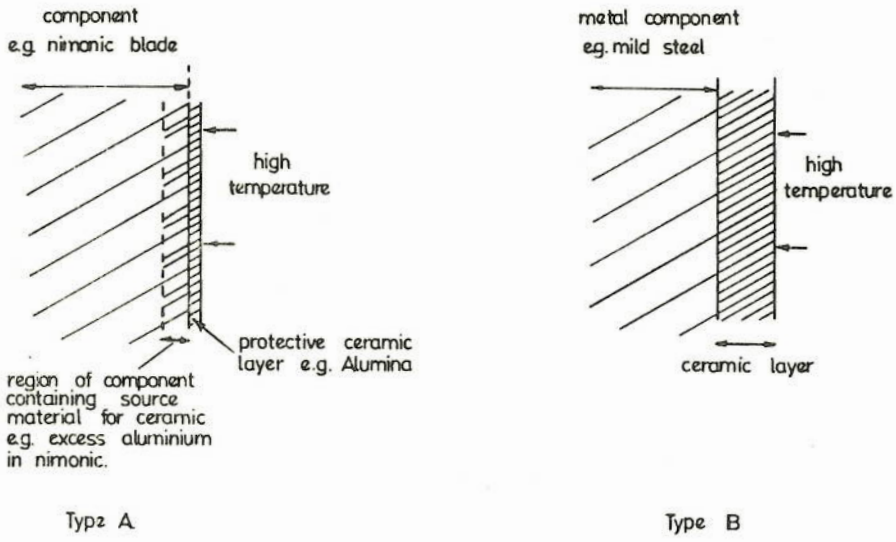


Figure 2. Basic apparatus.

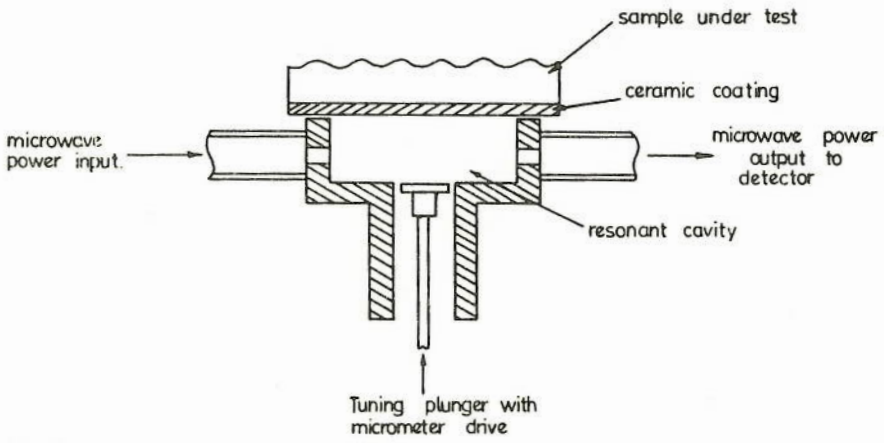


Figure 3. Microwave measuring apparatus.

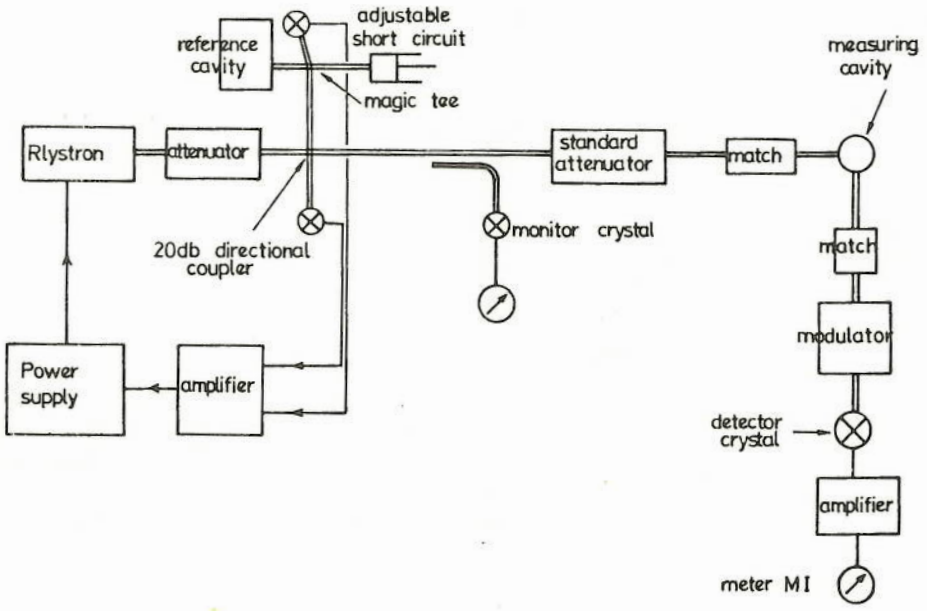


Figure 4a.

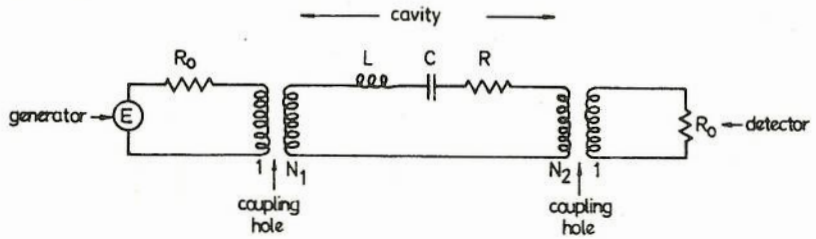


Figure 4b.

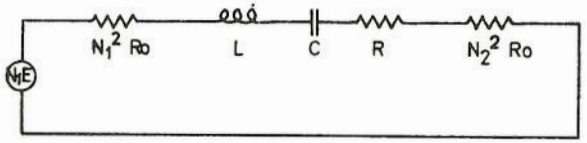


Figure 5. Generator voltage versus $\sqrt{\rho}$.

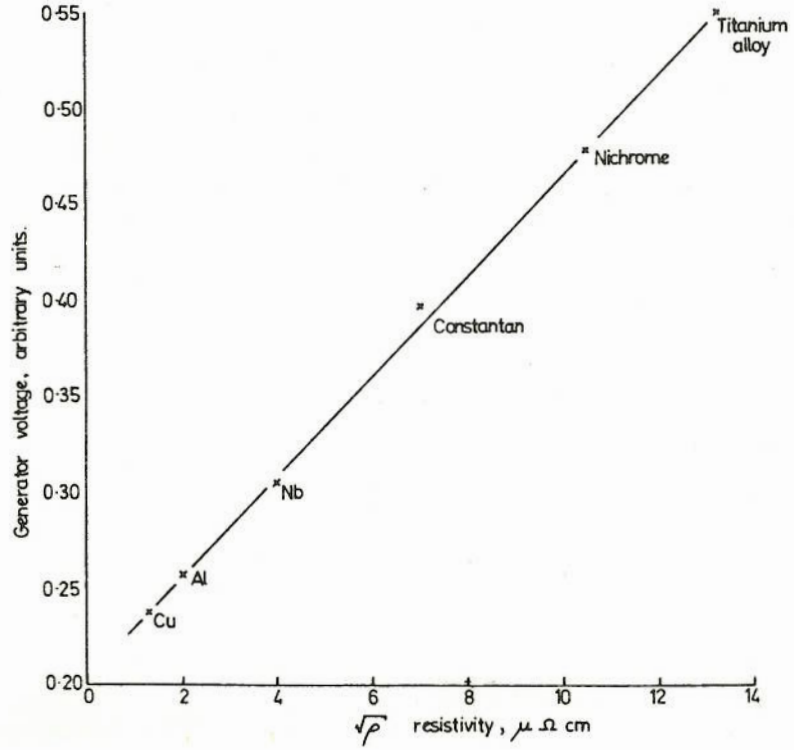


Figure 6. Variation of surface resistivity of disilicide coated niobium with time at 1250°C.

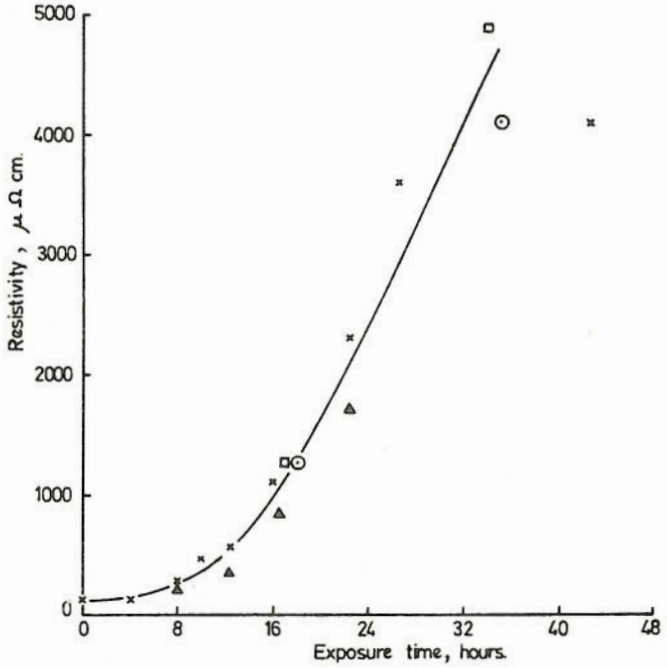


Figure 7. Variation of surface resistivity of disilicide coated niobium with time at 1000°C.

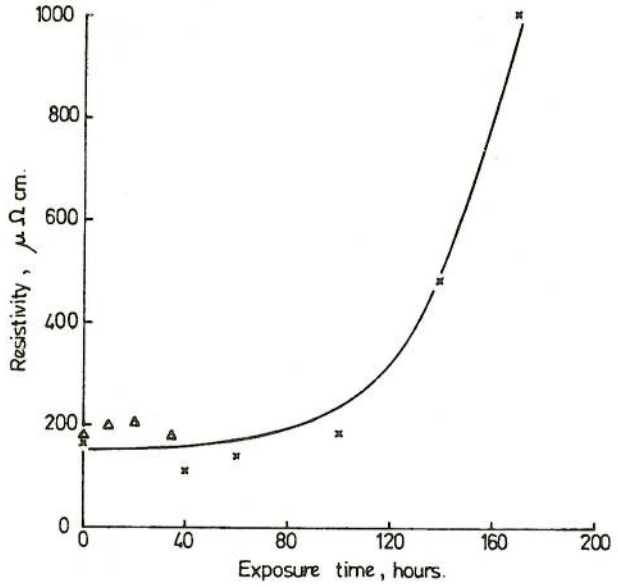


Figure 8. Variation of surface resistivity of disilicide coated niobium with time at 1450°C.

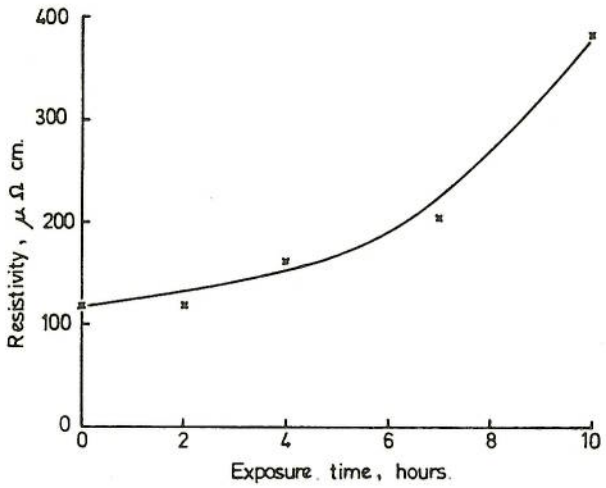


Figure 9.

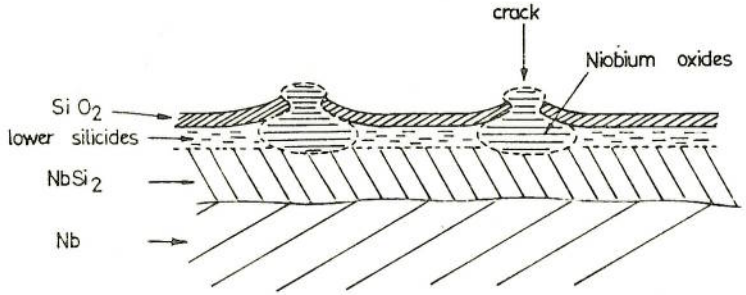


Figure 10. Oxide formation on mild steel at 1000°C.

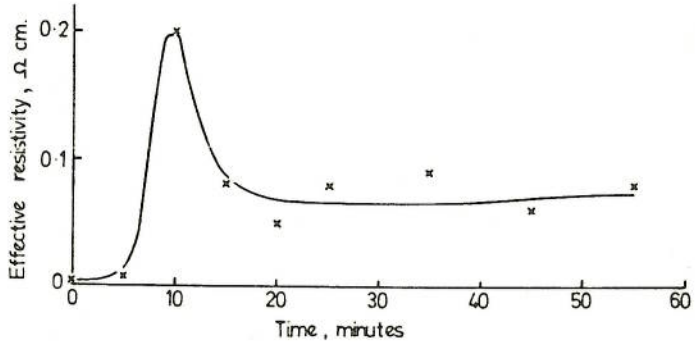


Figure 11. Initial changes in the resistivity of aluminised Nimonic at 1200°C.

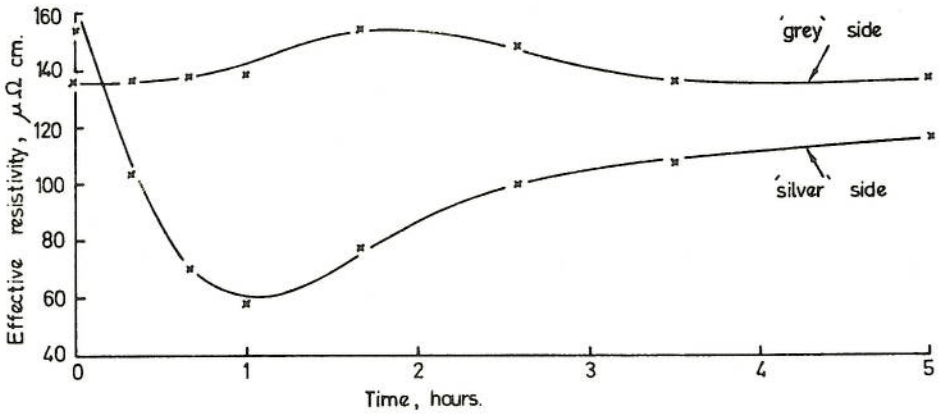


Figure 12. Long term changes in the resistivity of aluminised Nimonic at 1200°C.

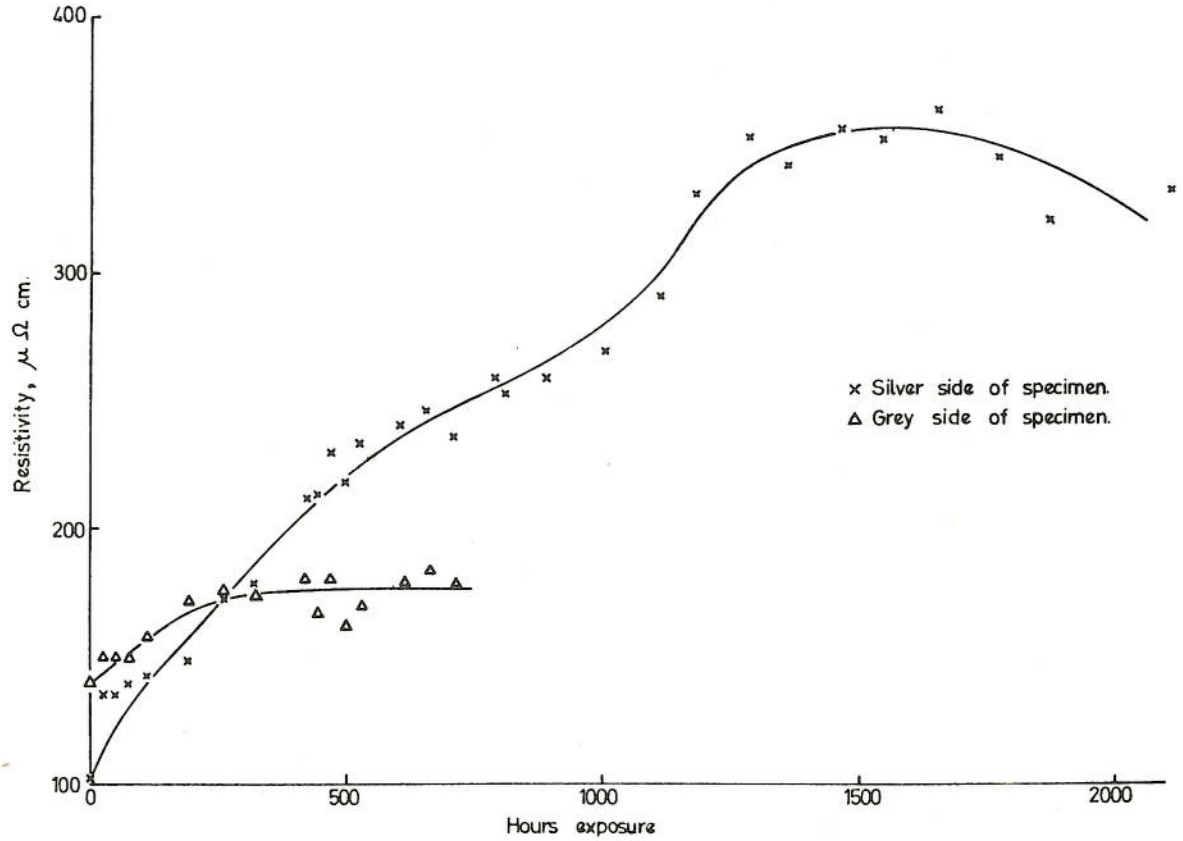


Figure 13. Long term changes in resistivity of aluminised Nimonic at 1000°C.

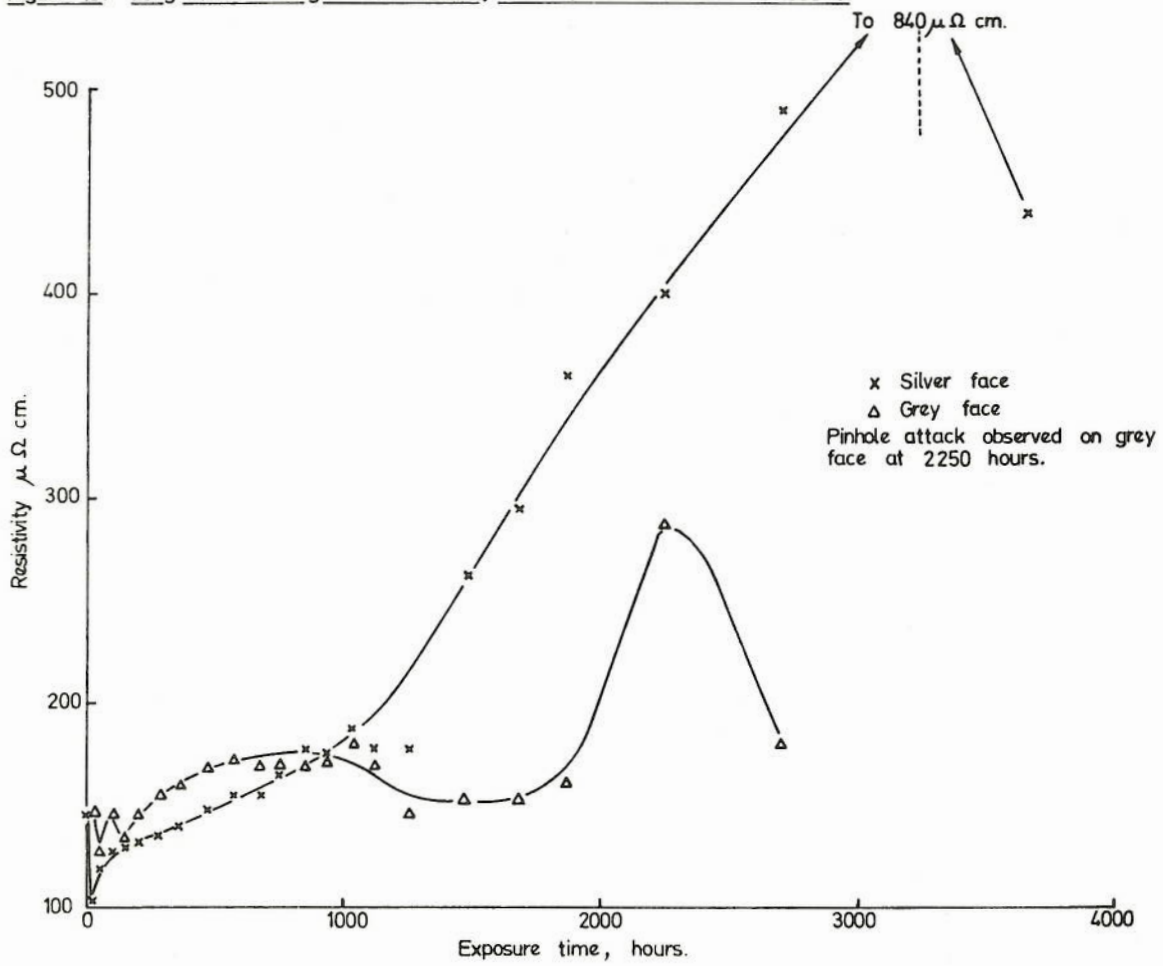
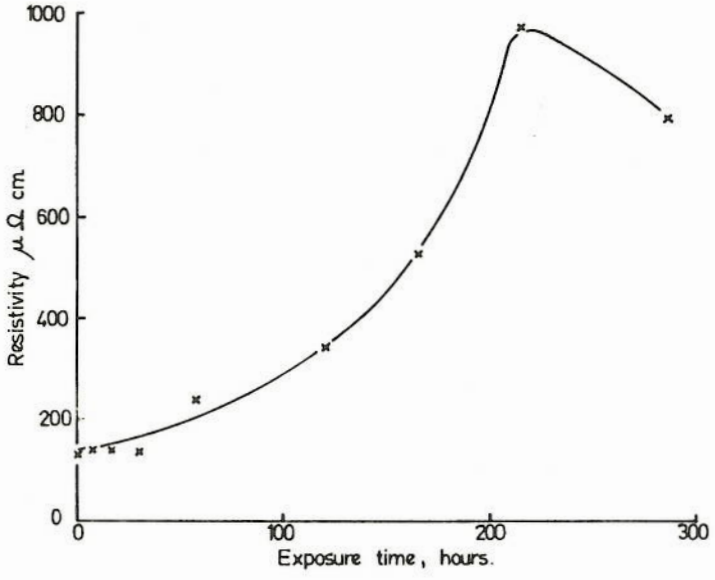


Figure 14. Variation resistivity of aluminised Nimonic at 1300°C.



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5. AUTHOR(S) (First name, middle initial, last name)

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